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Upgrading of Raw Gas from Biomass and Waste Gasification: Challenges and Opportunities

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Abstract The depletion of fossil fuel-based resources and concerns for increasing emissions of CO_2 call for new ways of producing environmentally-friendly substitutes for motor fuels and chemicals. Thermo-chemical conversion of biomass and waste using gasification is a strong candidate to meet these challenges. For efficient and cost-effective application of this technique, novel solutions for hot gas cleaning are needed. This review highlights some important areas for improvement of upgrading technologies for pressurised fluidised bed gasification systems using biomass as a fuel.

Keywords Gasification · Biomass · Upgrading · Gas cleaning · Catalyst · Process

1 Introduction

The modern society's long-term and still growing use of fossil fuels has resulted or will in the nearby future result in negative effects on the climate. Of particular concern is the increase of CO_2 content in the atmosphere, one of the major constituents promoting global warming [1]. Also, the dependency on fossil fuels is greatest in case of oil, which is a finite resource, which also raises questions in terms of supply security. The European Union (EU) published in 2010 the "European Strategic Energy Technology Plan (SET Plan)-Towards a low-carbon future" [2] stating that EU is to reduce the use of fossil fuel by 20%, reduce the CO_2 emissions by 20%, and increase the share of renewable energy to 20%, at 2020.

The world's main source of energy for the transport sector and production of chemicals is oil. In case of the transport sector, the use of fossil fuels was 47% of Europe's total consumption in 2006 [3]. The transport sector continues to increase in US and Europe, the growth in the emerging economies of India and China is estimated to be significantly larger, growing by at least 3% per year [4]. For example, in China the number of passenger cars is currently doubled every 4 years, but even with this amazing growth rate the World's greatest nation is way behind the car density in the USA. This growth also affects the emission of CO_2, where the transport sector is the only sector showing an increase over the past 20 years in Europe [5]. Chemicals are almost exclusively produced from fossil resources and approximately 4% of the oil worldwide is used for production of chemicals and plastics [6]. To address the dependency on oil in the transport and chemical sectors and to reduce the emission of CO_2, there is a need for alternative production chains of renewable substitutes, as well as combined actions such as changes in behaviour, changes in vehicle technology and development of public transportation [7]. An attractive solution for production of renewable substitutes is to replace petroleum and fossil based products in general with corresponding products produced from biomass.

Production of alternative renewable fuels, based on biomass, so-called biofuels, can be performed either by biochemical or thermo-chemical conversion. The thermo-chemical conversion is more efficient and superior in

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decomposing the organic compounds compared to biochemical processes [8]. Thermo-chemical conversion processes can mainly be divided into direct combustion, pyrolysis, gasification, and liquefaction [8]. To obtain a cost effective and economically feasible production of biofuel, the downstream biofuel synthesis and upgrading need to be as large as possible [9]. This implies a need for large quantities of syngas and the most suitable thermo-chemical conversion process to achieve large quantities of syngas is gasification.

In this article, the authors will present recent research and development within upgrading of raw gas from biomass and waste gasification focusing on selected new techniques for improved production of biofuels and chemicals. To narrow the scope, the article will focus on gasification systems, based on pressurised circulating fluidised bed gasification (PCFBG) technology, which is one of the techniques accepted for large scale thermo-chemical conversion of biomass [9].

2 Biomass and Waste Gasification

A number of different gasification systems exist for conversion of biomass and waste to produce transportation fuels as well as chemicals. The schematic in Fig. 1 illustrates the different possible applicable processes depending on fuel selected, gasification technology as well as downstream application. There are generally two gasification technologies suitable for production of high calorific syngas from biomass, either by using an entrained flow gasifier at a high temperature of 1300 °C, or using a fluidised bed gasifier together with a downstream catalytic reformer, both operating at around 900 °C [9]. The two technologies have different degree of maturity. Entrained flow gasifiers are a proven concept in case of coal as a fuel but biomass is not suitable to be directly injected to the reactor and therefore pre-treatments, such as torrefaction or pyrolysis are needed. In case of fluidised bed gasification, the technology is developed and already demonstrated with biomass for the production of heat and/or electricity. To achieve an economical, compact as well as an overall efficient conversion system for large scale production of transportation fuels and chemicals, pressurised systems are inevitable [10].

Typical process steps used for large scale PCFBG application will be described briefly below, including also brief basics of biomass and waste as fuels and gasification.

2.1 Biomass and Waste as Fuels

A range of different kinds of biomass and waste resources can be converted into fuels or heat and power. Table 1 illustrates the different characteristics of selected biomass and waste feedstocks.

In Table 1 only the mean values are shown, the standard deviation can be very large. The Phyllis database [11] contains more than 2,300 records of different compositions of biomass and waste materials and is open on the internet. The materials are divided into groups and subgroups containing information on the composition of biomass and waste. The principal differences are found in the ashes and moisture content. As a rule of thumb, waste fractions, like refuse derived fuel (RDF) and municipal solid waste (MSW) and non-organic residues, contain higher ash content than biomasses. Waste in form of plastics has generally higher energy content compared to biomass. The composition of a biomass is also significantly dependant on its origin, i.e., each and every batch of biomass/waste has its own specific characteristics, which in the end determines its performance as a fuel in the gasification plants [12]. The most important properties of gasification are elemental composition (H, C, O, N, etc.), ash content/composition, moisture content, heating value, bulk density and morphology, volatile matter, as well as inorganic content, such as Cl, S, N, alkalis and heavy metals. Important to note is that the ratio between C/H/O is at the same level for different biomasses if moisture and ash are excluded.

2.2 Gasification

2.2.1 *Basics of Biomass and Waste Gasification*

Gasification is a thermo-chemical process where a solid material containing carbon, such as biomass and waste, is chemically converted into gaseous products, during thermal treatment at high temperature in the presence of a gasifying agent. The temperature is in case of biomass typically between 600 and 1000 °C and the gasifying agent air, oxygen, steam, CO_2 or mixtures of these components [13]. Most biomass gasification systems utilize air or oxygen in partial oxidation or combustion processes. The produced gas is generally called producer gas and consists of CO, CO_2, H_2O, H_2, CH_4, other gaseous hydrocarbons, tars, char, inorganic constituents, and ash. The main chemical reactions taking place during the thermo-chemical conversion in a gasifier can be summarised as follows:

$$\text{Feedstocks} \rightarrow \text{char} + \text{tars} + CO_2 + H_2O + CH_4 + CO + H_2 + (C_2 - C_5) \quad (\text{endothermic}) \tag{1}$$

$$C + {}^1\!/_2\, O_2 \rightarrow CO \quad \Delta H_r^0 = -109\,\text{kJ/mol} \tag{2}$$

$$C + CO_2 \leftrightarrow 2CO \quad \Delta H_r^0 = +172\,\text{kJ/mol} \quad (\text{reverse Boudouard}) \tag{3}$$

$$C + H_2O \leftrightarrow CO + H_2 \quad \Delta H_r^0 = +131\ \text{kJ/mol} \quad (\text{Water gas reaction}) \tag{4}$$

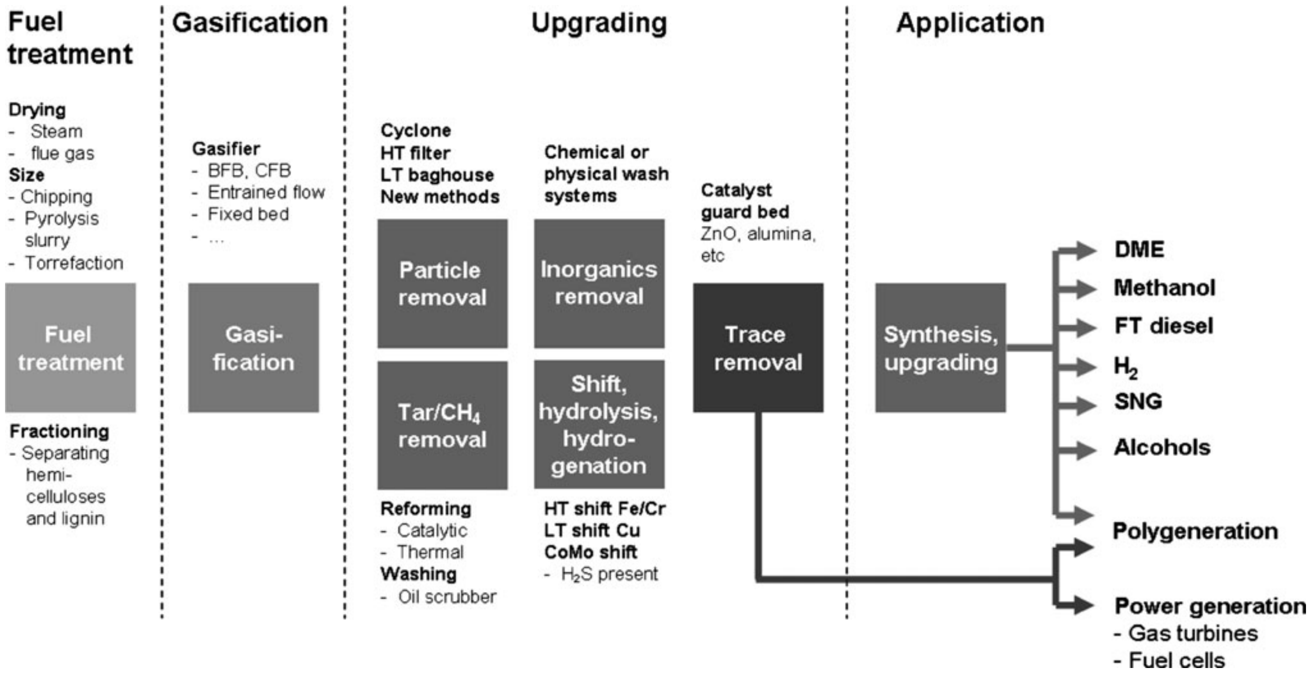

Fig. 1 Schematic illustrating the different steps and processes included in a gasification system

Table 1 Characteristics of selected biomass and waste fuels [11]

Group/sub group	H_2O cont wt%	Volatiles wt%	Ash wt% dry	LHV calc (MJ/kg)	C wt%	H wt%	O wt%	N wt%	S wt%	Cl wt%
RDF and MSW	14.6	88.7	17	22.9	54.8	8.12	34	0.94	0.4	0.72
Straw (stalk/cob/ear)	14.4	81.2	7.5	18.0	48.6	5.96	43.4	0.9	0.16	0.48
Untreated wood	18.7	82	2.2	18.8	50.7	6.06	42.8	0.36	0.06	0.05
Organic residue/product	25.2	85	10.5	18.9	49.3	6.52	41.8	2.36	0.63	0.34
Grass/plant	29.7	82.6	7	18.3	49.1	5.98	43.5	1.24	0.17	0.36
Non-organic residue	3.8	90.2	9.2	33.7	72.3	9.09	11.4	0.78	0.41	12.7
Algae	31.9	85.2	6.1	23.1	53.8	7.37	30.9	7.52	0.48	0.12
Chicken manure	42.1	82.8	20.6	17.5	49	6.61	38.8	5.09	1.06	–

$$\begin{aligned} &CH_4 + H_2O \leftrightarrow CO + 3H_2 \\ &\quad \Delta H_r^0 = +159\ \text{kJ/mol} \quad \text{(Steam reforming)} \end{aligned} \tag{5}$$

$$\begin{aligned} &CO + H_2O \leftrightarrow CO_2 + H_2 \\ &\quad \Delta H_r^0 = -42\ \text{kJ/mol} \quad \text{(Water gas shift).} \end{aligned} \tag{6}$$

The first step in the conversion using biomass as a feedstock is the thermo-chemical decomposition, called pyrolysis, of cellulose, hemicellulose and lignin to produce char and volatiles, expressed in reaction 1. Since biomass feedstocks tend to have a large fraction of volatile components (70–86% on a dry basis), pyrolysis is important in biomass gasification. The gasification of the pyrolysis products, converting some of the tars and the char into gas, is expressed in reactions 3 and 4. Heat needed for the endothermic reactions may be supplied internally in the gasifier by controlled partial combustion as expressed in reaction 2. Heat can also be provided externally by superheated steam, heated bed materials or by burning some of the char or gases separately [9]. The formed gaseous components may then undergo further reactions, such as steam reforming (5) or water gas shift (WGS) (6), within the gasifier, altering the gas composition of the final product gas leaving the gasifier.

The composition of the product gas from biomass gasification depends a great deal on the gasification process, the gasifying agent, and the biomass feedstock composition [14]. Of special importance is the choice of gasifying agent, since it has a great impact on the quality of gas, also affecting its suitability for different end-use applications after cleaning and upgrading to syngas. Gasification using air produces a gas, often called fuel gas, rich in nitrogen

Table 2 Gas components from oxygen/steam gasification of wood chips at 22 bar [16]

Product gas component	Vol%
H_2	14.8
CO_2	8.4
CO	20.3
CH_4	8.9
H_2O	47.0

(50–65%) and low in calorific value (4–8 MJ Nm^{-3}), mainly suitable as a fuel for gas turbines or combustion in conventional boilers [15]. When oxygen is used as the gasifying agent a syngas low in N_2 content and high in calorific value (10–18 MJ Nm^{-3}) suitable for other processes, such as hydrogen production, fuel cell feed, chemical and fuel synthesis, is produced [15]. A typical product gas composition from pressurised fluidised bed gasification using oxygen/steam as gasifying agent with an obtained caloric value of 13.8 MJ Nm^{-3} (dry) is exemplified in Table 2 [16].

The raw gas contains impurities in form of particulates, tar, and inorganic impurities, such as H_2S, CS_2, COS, AsH_3, PH_3, HCl, NH_3, HCN, and alkali salts, which have to be removed before utilising the gas depending on the application of interest. Of specific interest is the relatively large amount of tars produced, depending on the gasifier technique, feedstock used and process conditions. Tars are in case of gasification defined as condensable hydrocarbons, ranging from molecular weight above 78 (benzene) to molecular weight of above 300 [17] and can generally be divided into so-called water-soluble (phenolic) and non-water-soluble (aromatic) compounds [17].

The formation of tars is one of the main problems preventing the commercialization of the technology [18]. The tars may cause problems in downstream process equipment, such as blocking of pipes and filters. Even at very low concentrations, tars in the syngas may result in coking of catalysts in downstream gas upgrading processes [14].

2.2.2 *Pressurised Fluidised Bed Gasification*

Fluidised bed gasification (FBG) was originally developed for large scale coal gasification and later adapted to biomass to overcome the limitations with fixed bed gasification [12]. A fluidised bed is a unit where solid bed particles behave as a fluid through contact with a gas with a sufficient high gas velocity. The basics of fluidisation and related gasification techniques are out of the scope of this article and are described elsewhere [19].

The most promising FBG technology is based on circulating fluidised bed (CFB) gasifiers. The main advantages of CFB gasifiers are that they are suitable for fuels with high amounts of volatiles, have high fuel capacity, robust in case of fuel variations, have excellent particle/gas contact and fuel/bed heat transfer. General drawbacks are high tar and dust content of the produced gas, incomplete carbon conversion and a gas containing alkali metal compounds in their vapour state.

2.3 Upgrading of Raw Gas

For the majority of applications, the ideal syngas consists of H_2 and CO in a suitable ratio with a minor quantity of CO_2 also allowed. All impurities, as mentioned in the previous section, have to be removed. Nitrogen dilutes the syngas and is not desirable. By using oxygen as the gasifying agent, the content of nitrogen can be minimised. Examples of techniques for removal of impurities for typical PCFBG systems are briefly described below. More specific cleaning techniques are described in connection with applications in Sect. 3. Comprehensive reviews and books reviewing the subject are for example provided by Kumar et al. [13] and Higman and van der Burgt [20] and Iversen and Gøbel [21].

Particulate impurities in the raw gas from fluidised bed gasification typically consist of unconverted biomass material in form of ash (mineral components of the biomass) and char and bed material. The particulates in the gas may cause erosion of and plugging in downstream process equipments [18]. The most commonly used particulate removal technique for CFB gasification systems are cyclone separators, a natural component to recirculate the bed material to the reactor, for initial cleaning of larger particulates (>5 μm) and, barrier filters, either baghouse (woven ceramic, polymeric or natural fibres) at low temperatures below 350 °C or candle filters, metallic or ceramic, suitable for moderate to high temperatures up to 700 °C [13].

Tars can readily be removed from the gas using wet scrubbing and condensation to simultaneously remove water from the raw product gas. This produces large amount of wastewater with high organic content and also removes a large fraction of the carbon and hydrogen stored in the tars. Recently, a wet scrubbing technique, OLGA [22], using oil as the scrubbing media, has been developed to remove the tars (and also particulates) before syngas applications. The oil with tars can be recirculated to the gasifier and the energy in the tar is recovered. The disadvantage of this method is, however, the need for cooling the gas temperature prior to cleaning, decreasing the efficiency of the process.

For PCFBG syngas applications, primary mitigations, such as, optimisation of operational conditions, catalytic bed materials or additives [23], combined with secondary hot gas cleaning in the form of catalytic cracking, are identified as the preferred methods [9]. The catalytic cracking should be carried out at or near the gasifier temperature. This would improve the gas yield and reduce the organic load on waste water produced when the raw gas is cooled to remove steam from the raw product gas. In catalytic hot gas cleaning, the major catalytic materials considered, are calcined carbonate rocks (calcined dolomite, magnesite, calcite), and Ni, such as steam reforming catalysts or other Ni-based catalysts [24]. Due to the importance, several other possibilities have been investigated [18, 24]. Among the carbonate rocks, the dolomites are the most active materials. Dolomites are cheap and abundant, but are generally only suitable for use in fixed bed reactors due to the fragility of the materials, making them susceptible for erosion [25]. The dolomites are not active for reforming of methane in the product gas and are therefore not suitable for production of syngas production alone [24, 26]. The materials also readily react with chlorine, producing $CaCl_2$ with a relatively low melting point (782 °C), deactivating the surface. This makes the materials attractive as a guard bed protecting other downstream processes in case of using chlorine rich fuels. Ni-based materials are significantly more efficient in tar cracking compared to dolomites, active also in the case of methane reforming [26]. The materials can also be used in fluidised bed applications. However, the materials are rather expensive and are also easily poisoned by coke formation and by inorganics, such as S and Cl-containing compounds [18]. Improved Ni catalysts, using different supports and promoters, have reduced the problems with coking [18, 24, 26].

Alkali compounds are generally in vaporised form in the raw product gas, but condense at temperatures below 650 °C, forming particulates (<5 µm) in downstream equipment, and may also act as a poison for tar cracking catalysts as well as downstream conversion catalysts. Removal of alkali compounds can e.g., be carried out by cooling the gas below the condensation temperature and then removing the alkali particles with barrier filters [13]. Also, wet scrubbing methods can be effectively applied [21].

Other inorganic impurities, such as Cl and S-containing compunds, HCN, COS and ammonia, can be removed by means of physical and chemical washing methods. For example, the Rectisol process, using methanol as a solvent, can be applied to remove H_2S and COS, and simultaneously remove CO_2 from the syngas. Another example is the Selexol process, using dimethyl ethers of polyethylene glycol (DMPEG) [20]. Ammonia may be removed by catalytic destruction, using an iron-based catalyst, or by wet scrubbing [21].

Upgrading by means of shift, hydrolysis and hydrogenation are generally related to needs of the back-end applications and relevant aspects are therefore briefly described in Sect. 3 below.

In some cases, e.g., when Cu or Ni catalysts are used in the back-end application, also a guard bed ZnO, CuO or a mixture of the two, can be applied to remove H_2S to the very low levels required [20].

Table 3 Maximum accepted levels of catalyst poisons in reactant mixtures for chemical synthesis (adapted from [27])

Process/ Poisons	Sulphur	Halides	Nitrogen	Fe and Ni
Fischer–Tropsch	<1 ppmv	<10 ppb	<10 ppmv (NH_3) <0.2 ppmv (NO_x) <10 ppb (HCN)	–
Methanol	<0.5 ppmv <0.1 ppmv (COS)	<0.001 ppmv	–	<0.005 ppmv

3 Applications

In order to upgrade the raw product gas to a syngas, conforming to process specifications for production of chemicals and fuels, several clean-up steps are needed. Above in Table 3, the specifications regarding maximum concentrations of poisons for catalysts used in the methanol and Fischer–Tropsch (FT) processes are exemplified.

3.1 Examples of Applications

There are basically five different available technologies for motor fuel production from syngas: FT synthesis, methanol synthesis, dimethyl ether (DME) synthesis, higher alcohol synthesis and methanation (SNG – synthetic natural gas) [28, 29]. Some of these production processes will be discussed below. The common denominator between the various technologies is the need of syngas purification, due to the problem of catalyst deactivation. One of the most important catalyst deactivation mechanisms is sulphur poisoning [30], which will be discussed below. The H_2/CO ratio is also an important factor affecting the process design [31]. The raw gas from biomass gasification normally contains hydrogen and carbon monoxide of about the same levels of concentration. Consequently, the hydrogen concentration in the product gas must be increased by using water–gas shift or reforming units, if motor fuels or chemicals are going to be produced.

Sulphur is detrimental to the synthesis steps in the application, e.g., FT, DME or methanol. Due to the reducing conditions in the gasifier, most of the sulphur is present as H_2S accompanied by low concentrations of COS, CS_2 and various thiophenes [32]. The concentration of hydrogen sulphide in the raw gas can be up to 200 ppm [33]. The type and level of sulphur compounds in the gas

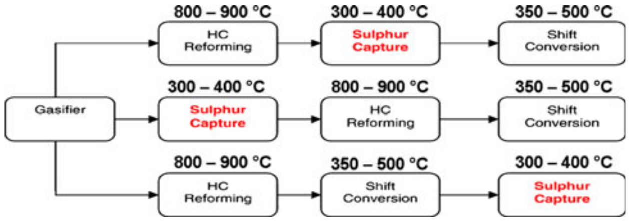

Fig. 2 Alternatives for installation of sulphur removal in gasification processes [34]

phase depends strongly on the operating parameters in the gasifier and the type of biomass used as feedstock. The synthesis catalyst will quickly be deactivated by strong chemisorption of sulphur on the active sites, resulting in severe poisoning. Depending on process conditions and the catalytic materials being used this poisoning can be reversible or irreversible.

The two sulphur removal alternatives that can be used are in situ sulphur removal or downstream processing. In downstream processing, the desulphurization step can be installed in various places in the process (see Fig. 2 above). If sulphur is removed after the water–gas shift step a lot of strain is put on the water–gas shift catalyst. Mixed metal oxides seem to be a viable alternative for abatement of H_2S and among them zinc titanates have been reported to be promising for commercial applications [33]. The type of gas clean-up technology being implemented strongly affects the process economy by influencing total efficiency and the need for auxiliary equipment by heating or cooling.

Below four examples of processes using synthesis gas from gasified biomass will be discussed where the focus is to produce motor fuels or chemicals.

3.1.1 *Fischer–Tropsch*

The first patent on the FT process was issued already in 1913 [35, 36], but the interest for the process has intensified during the last decade [37]. The FT process contains a heterogeneously catalyzed reaction where CO and H_2 are being chemisorbed on metallic surfaces, which are extremely sensitive to catalyst poisoning, especially sulphur (see discussion above). An important step is the dissociation of the carbon–oxygen bond. The FT synthesis produces a wide spectrum of hydrocarbons, where the product gas composition is strictly depending on the catalyst and operating parameters. While Fischer and Tropsch in the beginning were working on alkali-doped iron catalysts, modern FT synthesis catalysts are often based on cobalt promoted with for example rhenium. Re increases the reducibility of Co, increases Co dispersion and thereby improves FT synthesis activity [38].

Modern FT processes are focussed on producing long-chain linear hydrocarbons [30]. These FT waxes are subsequently being cracked into the product of choice. With this procedure, the process is suitable for production of sulphur-free diesel fuel with low aromatics content, which is a desirable product with continuously growing demand. This type of high-cetane clean diesel fuel allows the usage of advanced catalytic after-treatment methods using exhaust gas catalyst materials otherwise unsuitable for automotive applications. If the major product is gasoline, alkylation and isomerisation steps have to be included. Today the world's largest FT units based on solid fuel conversion to diesel and gasoline are Sasol 2 (operating since 1980) and Sasol 3 (since 1983) both in Secunda, South Africa [39]. A FT process based on biomass gasification would have a total efficiency of 35–40%.

3.1.2 *Synthetic Natural Gas (SNG)*

In synthetic natural gas production CO and CO_2 are being converted to methane by the two exothermic reactions below [40]:

$$2CO + 2\,H_2 \leftrightarrow CH_4 + \,CO_2 \quad \Delta H_r^0 = -247\ \mathrm{kJ/mol} \tag{7}$$

$$CO_2 + 4\,H_2 \leftrightarrow CH_4 + 2\,H_2O \quad \Delta H_r^0 = -165\ \mathrm{kJ/mol.} \tag{8}$$

The reactions are favored by low temperatures and high pressures. The synthesis catalyst of choice is nickel and the material is very sensitive to poisoning by sulphur and chlorine. The product gas leaving the methanation reactor is upgraded by using large-scale processes for CO_2 separation, such as Pressure Swing Adsorption (PSA), physical absorption by Selexol and the emerging technology membrane separation. In Fig. 3 a simplified process layout is given. The resulting SNG will typically after upgrading contain methane concentrations above 90 mol%. The resulting heating value of the SNG is normally above 33 MJ m^{-3} [28]. If the product gas is going to be used as motor fuel, the gas is further cleaned to almost pure methane. The international standards concerning fuels for biogas and natural gas vehicles are still being developed.

3.1.3 *Methanol*

The total efficiency for the methanol synthesis process is among the highest among all possible routes for syngas conversion. The economy for methanol production is very much dependent on the utilization of the large heat fluxes being produced by the exothermic process.

$$CO + 2H_2 \rightarrow CH_3OH(l) \quad \Delta H_r^0 = -128\ \mathrm{kJ/mol.} \tag{9}$$

While being a high-pressure process, when first commercialized by BASF in 1923, most of the methanol being produced uses a low pressure (5–10 MPa) and low temperature (220–280 °C) process first introduced by ICI. The highly active $Cu/ZnO/Al_2O_3$ catalyst is quite sensitive

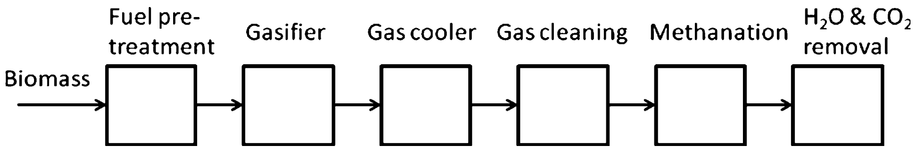

Fig. 3 Simplified schematic for the biomass to SNG process (adapted from [28])

to poisoning [41]. The Lurgi process uses a $Cu/ZnO/Cr_2O_3$ catalyst installed in a multi-tubular reactor, which gives a more isothermal temperature profile, and this is important for achieving high yields of methanol.

Most of the methanol being produced in the world is used for formaldehyde production. Methanol is an excellent fuel for spark-ignition engines with a high octane rating, but so far the use of methanol as motor fuel has been limited. One exception is the fleet tests performed in the 1980s and 1990s in Japan, USA, Germany and Sweden with both neat methanol and gasoline blends. Another important process is the production of MTBE for octane enhancement where isobutene and methanol are reacted over a catalyst. In this way methanol is used as an indirect motor fuel. Methanol can also itself be used as an octane booster. A third important product from methanol is acetic acid, which is produced by metal-catalyzed carbonylation using CO and makes up ca. 75% of the worldwide demand for acetic acid.

3.1.4 Methanol or DME to Olefins

The methanol-to-olefins (MTO) process is an intermediary step in the methanol-to-gasoline (MTG) process once launched by Mobil in the aftermath of the so-called oil crisis. The catalyst used was a zeolite catalyst called ZSM-5, which subsequently also became a common catalyst in research for reduction of nitrogen oxides in lean exhaust from vehicles. Also, shape-selective molecular sieve catalysts, such as SAPO-34, have drawn attention as possible candidates for large-scale production of olefins from methanol [42]. DME can also be converted to olefins using zeolite catalysts. In this case coking can be an issue plugging the pores of the catalyst [43].

4 Challenges and Opportunities

4.1 Challenges

So far there is not much large-scale experience of using biomass as feedstock for motor fuel production. Consequently, this process alternative has some inherent challenges, which will be discussed in this section. As in all multi-step processes, containing several clean-up units, the total efficiency depends on the heat management of the various steps. Many of the conventional gas filtering and catalytic conversion steps have optimum temperatures lower than the temperature in the gasifier. Often the temperature of operation is restricted by material issues. This implies that cooling is needed, which results in lower efficiency. Most of the technologies, which are available on the market have been developed for processing of coal or crude oil. Complicated gas cleaning systems involves high capital and running costs and also expensive maintenance. Solid waste, such as bed material, ash, sorbents and wastewater, all require handling costs. There is a trade-off between system efficiency and capital costs of the entire unit [9, 44]. Very efficient catalysts result in excessive costs, due to expensive gas cleaning. On the other hand, the downstream synthesis units will benefit from effective gas cleaning and prolong the lifetime of catalysts. This is especially valid for synthesis of FT diesel, methanol and DME. Principally, more deactivation-resistant catalytic materials are needed in the upgrading units. More durable Cu catalysts in the water–gas shift step would improve process economy, since this is a crucial step to increase the H_2/CO ratio needed for synthesis of motor fuels [45].

The main available technologies for gas cleaning in general operate at temperatures, which are lower than the temperature of the gasifier, implying the introduction of gas cooling equipment [20]. For PCFBG of biomass and waste the operating temperatures are in the interval 850–950 °C. Particulate removal at temperatures close to the operating temperature of the gasifier would be beneficial for the total efficiency. However, it is a challenge considering the corrosion and material fatigue problems occurring at high temperatures with gases containing sulphur, chlorine and alkaline compounds. Consequently, gas impurities need to be removed prior to filtration or alternatively novel methods for dust cake removal have to be introduced [46, 47]. The effects of poisons and trace impurities need to be examined more in depth. In addition to coking and sulphur poisoning, also other compounds can be present in the raw gas. Using biomass as feedstock will involve compounds, such as alkalis, chlorine, ammonia and other inorganic compounds [18]. A special attention has to be put on gasification of waste. This feedstock can contain substantial amounts of PVC and, hence, will produce HCl in the gasifier.

4.2 Opportunities: selected examples

One of the most important issues for efficient conversion is the development of hot gas cleaning at a temperature at or close to the temperature present in the gasifier. This includes development of novel particulate removal techniques, improved durable and robust catalysts for tar cracking and also new process schemes, including for the processes essential initial steps for producing a practically tar and particulate free product gas. The lifetime of traditional candle filters is limited by mechanical strains caused by tensile stresses due to the pressure drop across the filter and the reverse cleaning, high temperature corrosion, erosion, sealing system, thermal transient, as well as permanent deposition of ash [46]. The effects of these limitations become more severe at increased temperature reducing the lifetime. Additionally, the forced reverse cleaning also result in a minor penetration of fine particles and impurities through the filter since the dust cake where the efficient filtration occurs is removed. To improve the lifetime of traditional candle filters and possibly also increase the operational temperature, sorbents to remove impurities, such as alkalis, chlorine and sulphur, to favourable concentrations could be applied [47]. This would reduce the risks for weakening by high temperature corrosion. Alkalis could be removed in fixed beds with sorbents, such as, bentonites or bauxites [48, 49]. Sulphur and chlorine by adding sorbents, such as CaO [47], to be removed as CaS and $CaCl_2$ either in a fixed bed or a cyclone, upstream the particulate candle filter.

A promising example to overcome the limitations present in traditional high temperature ceramic candle filters is filtration, based on a novel pulse less filter technology, proposed by Sharma et al. [47]. The novel concept shown in Fig. 4 uses an in line jet ejector to produce a very high annular (or shear) velocity on the filter surfaces to control the cake thickness by forcing a removal of ash particles as well as providing continuous seepage flow of gas through the filter. Experimental results show that a thin continuous dust layer is retained during filtration minimising breakthrough of fine particles and impurities as well as most likely protect the filter surface from erosion and corrosion.

One way to improve efficiency in the hot gas cleaning and thus also reduce the costs is to reduce the number of steps in the overall process by combining different physical and chemical processes in the same equipment. An interesting example is to integrate catalytic tar cracking in a barrier particulate filter. This was first proposed for combustion applications by Saracco and Montanaro [50] and further elaborated to gasification applications by research groups at Vrije Universiteit Brussel, Belgium [51–55], University of L'Aquila, Italy [56, 57] and TU Delft, The Netherlands [58], all in cooperation with Pall Filtersystems GmbH Werk Schumacher, Crailsheim, Germany. Schematics of two different designs, (a) deposits of Ni/MgO catalyst onto the pore walls in α-alumina in a candle [52] and (b) a catalytically active fixed bed in a cylindrical catalytic filter element [53], are shown in Fig. 5. Recently, the fixed bed design catalytic candle filter, using Ni catalyst on MgO particle supports, was compared with different layered catalytically active ceramic SiC candle filters, impregnated with different proportions of Al_2O_3 and MgO together with other compounds as precursors for a layer of Ni. The fixed bed design showed superior catalytic performance than most of the catalytically active layered candle filters. A complete naphthalene conversion at 800 °C in a 50 h test in the presence of 100 ppmv H_2S was observed.

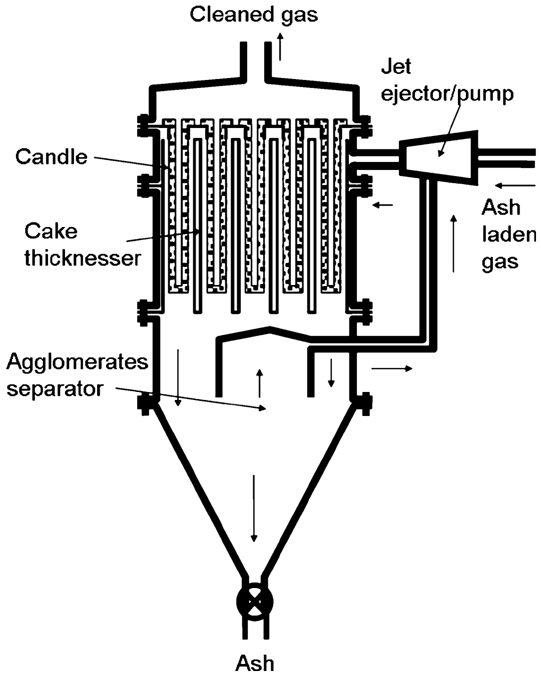

Fig. 4 Conceptual design of a full scale pulse less filter unit including a jet injector (adapted from [47])

Sharma et al. [47], also mentioned the possibility to integrate catalytically active filter elements in pulse less filters, combining a durable filter concept with tar cracking abilities at higher temperatures than possible today.

Application of catalytically active candle filters in gasification using problematic fuels, such as waste, producing a raw product gas with high chlorine content, would need a development of catalysts not sensitive to chlorine. Nordgreen et al. [59, 60] have shown that metallic iron in form of sinter is catalytically active for tar cracking. Metallic iron will not react with chlorine and could easily be sintered to various filter elements for application in hot gas cleaning.

There is an interesting development going on in chemical industry, which is sometimes referred to as process intensification [61]. This includes for example integrating synthesis and separation steps, heat integration with advanced heat exchanger technologies to increase heat transfer rates, catalytic coating of heat exchanger surfaces, and the usage of microchannel reactors to overcome mass transfer

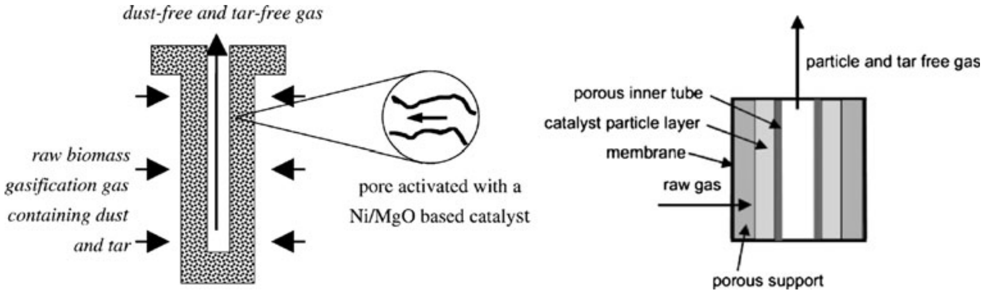

Fig. 5 Schematic designs of **a** a α-alumina based candle with catalyst deposited onto the pore walls [52] and **b** a cylindrical layer fixed bed based catalytic filter element [53]

resistance and increase reaction rates. The latter option would be favored by using microreactor technologies [62]. Another interesting option is to couple endothermic and exothermic reactions by utilizing the inherent energy content in the feedstock to promote for example reforming reactions [63]. In chemical industry new interesting reformer concepts are currently being evaluated. One of them is convective reforming, which helps overcoming the constraints connected with conventional tubular reformers [64].

The FT process is interesting with its inherent possibilities to customize sulphur-free products for various demands. One example is mobile fuel cell applications (e.g., fuel cell auxiliary power units), where FT could play a major role in supplying vehicles with clean fuel cell quality diesel fuels in the future. However, the most important application will be as high-cetane diesel fuel for future low-emission trucks and passenger cars, where the demand is continuously increasing. The possibility to control the process to yield products with low contents of polyaromatics, aromatics and olefins is very attractive. However, the process uses a lot of energy and is in need of the development of more active catalytic materials and efficient engineering solutions. Gasified biomass normally has a H_2/CO ratio below 1 [65]. This means that more hydrogen has to be added to be able to run the FT synthesis, which requires a value exceeding 2 [66]. An integration of the water–gas shift step to adjust the H_2/CO ratio to the process conditions would be favorable to increase the efficiency of the process. One possibility would be to promote a material possessing low cost and high water–gas shift activity, such as iron, with alkali compounds. However, the activity for FT synthesis is not as high as for example cobalt-based materials. It is certainly a delicate balance to run an integrated FT + WGS process, since there is always a risk of losing CO due to an excessively high water–gas shift activity of the combined catalyst. The CO will then be converted to CO_2 instead of to the valuable hydrocarbon [67]. A novel approach is to use microstructured reactors, which can circumvent the problem with rapid temperature increases when using highly active catalysts and thereby counteract catalyst deactivation [68].

5 Concluding Remarks

To address the dependency on oil in the transport and chemical sectors and to reduce the emission of CO_2, there is a need for alternative production chains of renewable substitutes, as well as combined actions such as changes in behaviour, changes in vehicle technology and development of public transportation. At the same time, the urbanization and rapid development in the BRIC countries (Brazil, Russia, India and China) and also in other rapidly developing areas will worsen these problems. An attractive solution for production of renewable substitutes is to replace petroleum and fossil based products in general with corresponding products produced from biomass. A feasible solution for production of alternative renewable fuel and chemicals is thermo-chemical conversion using pressurised fluidised bed gasification techniques. A challenge, using these techniques, is the upgrading of the raw gas produced in the gasification unit using waste and biomass as feedstocks. These raw materials often contain high contents of problematic impurities, such as alkalis, sulphur and chlorine. As in all multi-step processes, containing several clean-up units, the total efficiency depends on the heat management of the various steps. Many of the conventional gas filtering and catalytic conversion steps have optimum temperatures lower than the temperature in the gasifier. This calls for the introduction of novel technologies in areas, such as filtration at higher temperatures, more durable catalysts and a higher degree of process integration. The temperature for a particular upgrading system should be as high as possible in the upgrading steps. However, the temperature of the clean syngas always needs to be adjusted to the requirements of the downstream application.

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Happy Birthday Anders! We hope for many more prosperous years in catalysis, as well as in cross-country skiing in the beautiful Norwegian mountains.

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